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Functionalized Cyclic Disilenes via Ring Expansion of Cyclotrisilenes with Isocyanides

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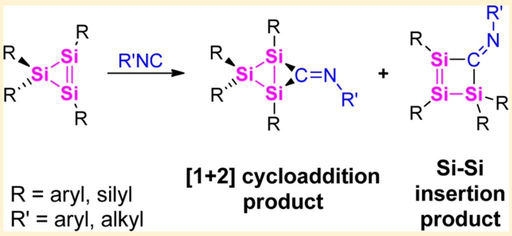
Supporting Information

ABSTRACT: The reaction of cyclotrisilenes **1** with 1 equiv of alkyl and aryl isocyanides at 25 °C affords the four-membered trisilacyclobutenes **2** with an exocyclic imine functionality as the major products of formal insertion into one of the Si–Si single bonds of **1**. Minor quantities of the iminotrisilabicyclo[1.1.0]butanes **3** are obtained as side products, formally resulting from [1 + 2] cycloaddition of the isocyanides to the Si–Si double bond of **1**. The bicyclo[1.1.0]butanes **3** become dominant at lower temperatures and may react with an additional 1 equiv of isonitriles to give the diiminotrisilabicyclo[1.1.1]pentanes **4**.

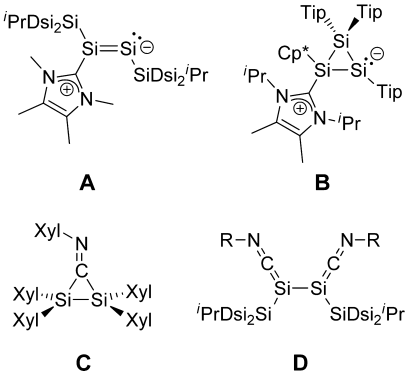


The chemistry of silicon multiple bonds has matured dramatically in the past few decades.[1] Even functionalized disilenes (Si$=$Si) and silenes (Si$=$C) are becoming increasingly available and show considerable promise as synthetic tools for the transfer of intact silicon-containing double-bond moieties.[2] Conversely, small, unsaturated silacycles[3] are relatively rare due to their less straightforward synthesis. To date, the few known examples have been obtained by the reduction of halosilanes,[4] reactions of metallosilyl reagents,[5] cycloadditions of disilynes with alkenes,[6] and thermal or photochemical interconversions.[7] In particular, cyclotrisilenes are attractive precursors: the incorporation of the silicon-containing double bond into the highly strained three-membered ring allows for functionalizing interventions via ring opening.[5b,d,7c]

The relatively shallow energy profile of species with silicon–silicon multiple bonds manifests itself in the facile polarizability of electron density,[8,9] which makes disilenes and disilynes susceptible to coordination by strong Lewis bases. The coordination of an N-heterocyclic carbene (NHC)[10] to the $Si\equiv Si$ bond of a bulky silyl-substituted disilyne[9] affords complex **A** (Scheme 1), thus generating a nonbonding electron pair at the second silicon atom available for further functionalization: e.g., with ZnCl$_2$.[11] Another remarkable example was very recently reported by Scheschkewitz and Jutzi et al. with the reversible coordination of cyclotrisilene Tip$_3$Cp*Si$_3$ (Tip = 2,4,6-^{i}Pr$_3$C$_6$H$_2$) to give the corresponding cyclotrisilene–NHC complex **B**.[5b]

Previously, West and co-workers reported that the reaction of tetraxylyldisilene R$_2$Si$=$SiR$_2$ (R = Xyl = 2,6-dimethylphenyl) with XylNC yields the [2 + 1] cycloaddition adduct **C** as the sole product.[12] Very recently, the Scheschkewitz group reported the reaction of the unsymmetrically substituted disilene Tip$_2$Si$=$Si(Ph)Tip[13] with isocyanides to initially yield a similar adduct.[14] The differing coordination modes in **B** and **C** can be regarded as a reflection of the stronger π-accepting character of the isocyanide in comparison to NHCs. This interpretation is lent additional support by the reaction of a disilyne[9] with alkyl isocyanides to afford the disilyne–isocyanide adducts **D**, which are best described as bis(silaketenimines), highly functional unsaturated silicon compounds.[15]

Scheme 1. Adducts between Si$=$Si and $Si\equiv Si$ Species and N-Heterocyclic Carbenes or Isocyanides[a]



[a]Legend: **A**, Dsi = CH(SiMe$_3$)$_2$; **B**, Tip = 2,4,6-^{i}Pr$_3$C$_6$H$_2$, Cp* = 1,2,3,4,5-pentamethylcyclopentadienyl; **C**, Xyl = 2,6-Me$_2$C$_6$H$_3$; **D**, Dsi = CH(SiMe$_3$)$_2$, R = ^{t}Bu, ^{t}Oct.

Bearing in mind the high strain in cyclotrisilenes, we decided to investigate the coordinative properties of isocyanides toward aryl- and silyl-substituted representatives of this class of

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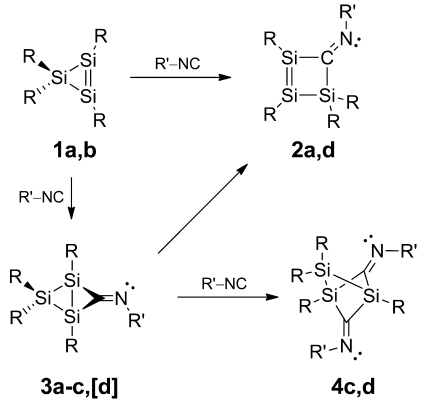
compounds: **1a** with triisopropylphenyl (Tip) substituents and **1b**[5b] with Me^{t}Bu$_2$Si groups.[4b] Here we report the reactions of alkyl and aryl isocyanides with cyclotrisilenes **1a,b** affording the four-membered cyclic disilenes **2a,d** with an exocyclic imine functionality in potential conjugation with the Si═Si double bond. In addition, the isomeric bicyclic imines **3a–c** were isolated as potential intermediates as well as representative examples (**4c,d**) of reaction products with a second equivalent of isocyanide.

Cycloaddition Reactions of Isocyanides with Cyclotrisilenes. Treatment of cyclotrisilenes **1a,b** with 1 equiv of xylyl or cyclohexyl isocyanide, respectively, resulted in formation of the bicyclic compounds **3a–c** (Scheme 2).

Scheme 2. Reactions of iIocyanides with Cyclotrisilenes[a]



[a] Legend: **1a**, R = Tip = 2,4,6-^{i}PrC$_6$H$_2$; **1b**, R = SiMe^{t}Bu$_2$; **2a**, R = Tip, R′ = ^{t}Bu; **2d**, R = SiMe^{t}Bu$_2$, R′ = Xyl = 2,6-Me$_2$C$_6$H$_3$; **3a**, R = Tip, R′ = ^{t}Bu; **3b**, R = Tip, R′ = Xyl; **3c**, R = SiMe^{t}Bu$_2$, R′ = cyclohexyl = Cy; [**3d**], R = SiMe^{t}Bu$_2$, R′ = Xyl; **4c**, R = SiMe^{t}Bu$_2$, R′ = Cy; **4d**, R = SiMe^{t}Bu$_2$, R′ = Xyl.

Compound **3a** was obtained as a powder of near-spectroscopic purity by evaporation of the solvent (hexane) in 77% yield; **3b,c** crystallize in good yields (**3b**, 85% **3c**, 58%) from hexane or pentane, respectively. The ^{29}Si NMR spectra of **3a,b** exhibit each two signals at relatively low field and one at higher field (**3a**, δ −17.42, −25.05, −91.49; **3b**, δ 40.5, 27.9, and −78.7 ppm). In both cases, the two lower field resonances are extremely broad and are assigned to the bridgehead silicon atoms, while the high-field resonance is due to the Tip$_2$Si group. The silyl-substituted product **3c** shows a similar NMR spectrum, albeit with all three resonances shifted to substantially higher field (δ −93.9, −105.4, and −127.9 ppm). Again, the two high-field resonances are assigned to the bridging silicon atoms. The chemical inequivalence of all three silicon atoms in **3a–c** is readily explained by the presence of the exocyclic imine functionality: the bridgehead atoms are located in *E* and *Z* positions relative to the substituent at the imine nitrogen atom. The imine ^{13}C resonances of **3a–c** are found at low field, as is usual for cyclic bis(silyl)imines[12] (**3a**, δ 180.8; **3b**, 193.2; **3c**, 198.2 ppm).

Single crystals of **3b,c** were obtained from hexane and pentane, respectively. X-ray crystallography confirmed the formulation of the two compounds as the products of formal [2 + 1] cycloadditions between **1** and isocyanides. The structure of **3c** suffers from severe disorder (details are given in the Supporting Information); therefore, only the structure of **3b** will be discussed here.[16] Compound **3b** crystallized as the hexane solvate at room temperature (Figure 1). The folded bicyclobutane-type structure exhibits a long bond between the two bridgehead atoms: Si2–Si3 = 2.4255(6) Å. The fold angle between the plane of the trisilacyclopropane and the disilacyclopropanimine ring is 134.2°. The two bonds between the bridgehead silicon atoms and the imine carbon have essentially identical distances (Si2–C1 = 1.8667(16) Å, Si3–C1 = 1.8681(16) Å). The imine C1–N1 double-bond distance is unremarkable at 1.282(2) Å.[17]

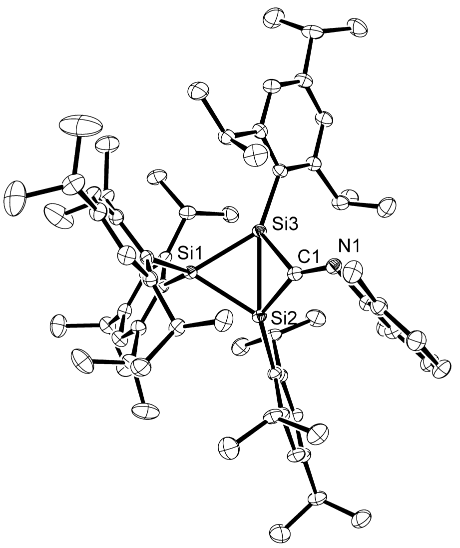


Figure 1. ORTEP diagram of **3b**·C$_6$H$_{14}$ (ellipsoids at the 50% probability level). Hydrogen atoms and hexane solvent molecule are omitted for clarity. Selected bond distances (Å): Si1–Si2 = 2.3264(6), Si1–Si3 = 2.2905(6), Si2–Si3 = 2.4255(6), Si2–C1 = 1.8667(16), Si3–C1 = 1.8681(16), C1–N1 = 1.282(2). Selected bond angles (deg): Si1–Si2–Si3 = 57.589(17), Si1–Si3–Si2 = 59.034(18), Si3–Si1–Si2 = 63.377(19), C1–Si2–Si3 = 49.53(5), C1–Si3–Si2 = 49.48(5), Si2–C1–Si3 = 81.00(6).

The formal [2 + 1] cycloaddition reactions of isocyanides yielding **3b,c** are akin to the aforementioned reaction by West and co-workers, forming the disilacyclopropanimine **C**.[12] Indeed, the solid-state structure of **3b** bears close similarities to that of **C**; the disilacyclopropane ring and the exocyclic C═N double bond of **3b** are virtually coplanar (dihedral angle 13.4°; for **C** this is reported as "∼13°"), and the *N*-xylyl group is orthogonal to the C═N double bond in both compounds. Despite the similar aryl substituents, the bridging Si–Si bond in **3b** is significantly longer than the equivalent bond in **C** (2.4255(6) Å vs 2.328(3) Å), presumably due to the significantly increased ring strain arising from the bicyclobutane structure of **3b**. Despite the ring strain and long bridging bond, the two bridgehead silicon atoms of **3b** possess chemical shifts (δ 40.5, 27.9) in the same region of the ^{29}Si NMR spectrum as for the equivalent atoms in **C** (δ 37.2 ppm).

When the silyl-substituted cyclotrisilene **1b** is reacted with 2 equiv of cyclohexyl isocyanide, the diiminotrisilabicyclo[1.1.1]-pentane **4c** is formed, presumably via a second equivalent of isocyanide reacting with **3c** at the strained Si–Si bridging bond (Scheme 2). Compound **4c** has two resonances in the ^{29}Si NMR spectrum at δ −19.4 and −108.1 ppm, reflecting its higher symmetry in comparison to **3c**. A single resonance for the two imine carbon atoms was detected at δ 194.2 ppm in the ^{13}C NMR spectrum.

Iminotrisilacyclobutenes. When the cyclotrisilenes **1a**,**b** were reacted with *tert*-butyl and xylyl isocyanide, respectively, divergent reactivity was observed. Addition of xylyl isocyanide to solutions of **1b** at room temperature afforded the ring-expanded iminotrisilacyclobutene **2d** as dark red crystals in moderate (48%) yield (Scheme 2). Similarly, **2a** was formed via the reaction of **1a** with ^{t}BuNC at 60 °C for 16 h. In the ^{29}Si NMR spectrum of **2b**, two low-field resonances (δ 173.9 and 165.1 ppm) are characteristic of the presence of a silyl-substituted Si═Si double bond, although these values are somewhat downfield in comparison with other four-membered disilenes (with chemical shifts between δ 141.3 and 167.6 ppm).[4a,6,18] The imino carbon atom was observed at δ 206.7 ppm in the ^{13}C NMR spectrum, in the same region as that for **3** and **4**. The ^{29}Si NMR spectrum of the Tip-substituted **2a** reveals two signals at δ 131.63 and 82.77 ppm for the Si═Si double bond, upfield of those observed for **2b**, as would be expected for an aryl-substituted disilene in comparison to a silyl-substituted example. The four-coordinate silicon atom is found at δ −11.86 ppm. In the ^{13}C NMR spectrum, the imino carbon shows a resonance in the typical downfield region at δ 194.8 ppm.

The molecular structures of **2a** (see the Supporting Information) and **2d** in the solid state were determined by single-crystal X-ray diffraction analyses (Figure 2). The four-membered rings of the two compounds are almost planar, with the sum of the internal angles being close to 360° (**2a**, 358.9°; **2d**, 358.7°). For **2d**, the Si═Si and C═N double bonds lie in the same plane, as seen from the values for the sum of angles at Si1, Si2, and C1, which are all close to 360°. In **2a**, the C═N bond lies somewhat out of the plane of the Si═Si double bond, with an angle of 9.6° between the plane defined by C−N═C and that defined by the four ring atoms. Despite the coplanarity of the Si═Si and C═N double bonds in **2d**, the bond lengths of Si═Si (2.1975(7) Å) and C═N (1.286(2) Å) are very similar to those observed in other four-membered cyclic disilenes (2.163−2.174 Å)[4a,6,18] and nonconjugated imines C═N (1.279 Å).[17] Moreover, the skeletal Si1−C1 bond length of 1.9169(18) Å is very similar to that of the single Si−C bonds in the bicyclo[1.1.0]trisilabutane derivatives (1.906−1.920 Å).[7a] For **2a**, the Si═Si and C═N double-bond lengths (2.1505(6) and 1.279(2) Å, respectively) are both slightly shorter than those observed for **2d**, as is the Si═Si−C single bond at 1.906(2) Å.

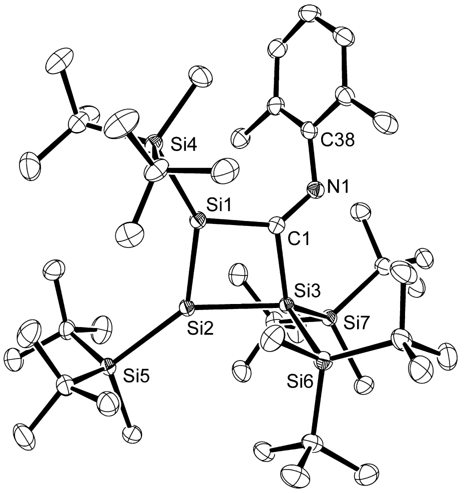


Figure 2. ORTEP diagram of **2d** (50% probability level). Hydrogen atoms are omitted for clarity. Selected bond distances (Å): Si1−Si2 = 2.1975(7), Si1−C1 = 1.9169(18), Si2−Si3 = 2.3835(7), Si3−C1 = 1.9567(18), N1−C1 = 1.286(2). Selected bond angles (deg): Si2−Si1−Si4 = 142.95(3), Si2−Si1−C1 = 88.91(6), Si4−Si1−C1 = 125.78(6), Si1−Si2−Si3 = 83.26(2), Si1−Si2−Si5 = 134.78(3), Si3−Si2−Si5 = 141.93(3), Si2−Si3−Si6 = 103.89(2), Si2−Si3−Si7 = 122.04(3), Si6−Si3−Si7 = 118.52(3), Si2−Si3−C1 = 82.81(5), Si6−Si3−C1 = 111.27(5), Si7−Si3−C1 = 112.83(5), C1−N1−C38 = 125.51(15), Si1−C1−Si3 = 103.72(8), Si1−C1−N1 = 135.10(14), Si3−C1−N1 = 120.66(13).

Despite the relative coplanarity of the Si═Si and C═N double bonds in **2a**,**d**, there is no clear structural evidence for conjugation. We therefore recorded UV−vis spectra of **2a**,**d** in hexane to further clarify the issue. While solutions of **2a** are bright yellow, with an absorbance at λ_{max} 402 nm fairly typical of an aryl-substituted disilene, **2d** is deep red. The UV−vis absorption spectrum of **2d** in hexane has a strong absorption at 455 nm (ε = 11000 cm^{2} mol^{-1}), which was assigned to the π−π* (Si═Si) electronic transition by TD-DFT calculations. This absorption has a shoulder corresponding to the n (lone pair on nitrogen) to π* (Si═Si) forbidden transition. The maximum wavelength of **2d** is very close to that of other four-membered disilenes (420−455 nm).[4a,6,18]

The possibility of Si═Si and C═N conjugation in **2d** was also examined by DFT calculations at the B3LYP/6-31G(d) level on the model compound **IIb** (in which the SiMe^{t}Bu$_2$ groups of **2d** are replaced by SiMe$_3$ groups). The optimized structural parameters of **IIb** are in good agreement with the X-ray crystallographic data for **2d**.

The molecular orbitals of **IIb** (Figure 3) show that the HOMO consists of the Si−Si π bond and some minor contributions from the Si−SiMe$_3$ σ bonds. The LUMO consists of the π* orbital of the Si═Si bond slightly mixed with the π* orbital of the C═N bond. The C═N π bonding orbital is primarily located in the HOMO−15. These computational results are consistent with both the spectroscopic and structural properties of **2d**, which indicate only minor interactions between the Si═Si and C═N double bonds.

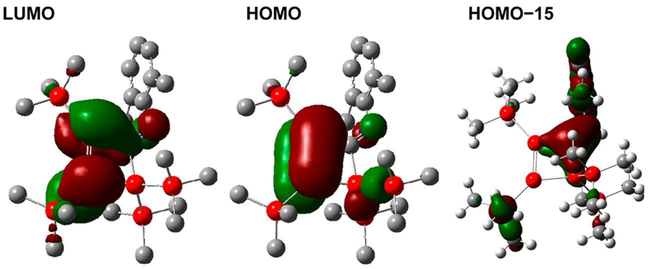


Figure 3. Relevant molecular orbitals of **IIb**.

Mechanism for the Formation of 2a,d. In an attempt to understand the factors controlling formation of the iminobicyclobutane products **3** vs the iminocyclobutenes **2**, calculations on the model compounds iminobicyclobutane **I** and iminocyclobutene **II** were performed at the B3LYP/6-31G(d) level (Figure 4). Model compounds **IIa**,**b**, bearing alkyl and aryl substituents, respectively, at nitrogen, are both found to be more stable than their bicyclobutane isomers **I**, with the aryl-substituted cyclobutene **IIb** showing the greater relative stability vs its bicyclobutane isomer (**IIa**, −2.4 kcal mol^{-1} vs **Ia**; **IIb**, −5.1 kcal mol^{-1} vs **Ib**). These results suggest that the

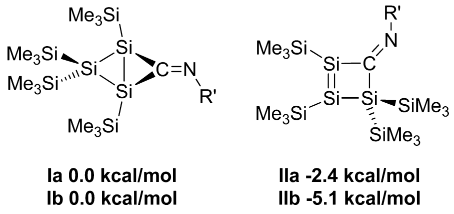


Figure 4. Relative energies of trimethylsilyl-substituted Si$_3$C bicyclo[1.1.0]butanes **I** and cyclobutenes **II** (optimized at the B3LYP/6-31G(d) level): **Ia**, **IIa**, R′ = Cy; **Ib**, **IIb**, R′ = xylyl.

product of the reactions with **1b** and isocyanides is formed under kinetic control. In the case of xylyl isocyanide, the thermodynamic product **2d** is generated, while with cyclohexyl isocyanide the reaction stops at the iminobicyclobutane **3c**. In order to confirm this hypothesis, xylyl isocyanide was reacted with **1b** at −30 °C. The sole product isolated was the iminotrisilabicyclo[1.1.1]pentane **4d** (the 2:1 adduct), not the trisilacyclobutene **2d**. Because of its thermal instability, compound **4d** must be characterized by low-temperature NMR and X-ray diffraction analysis,[16] which reveal spectroscopic and structural parameters very similar to those for **4c** (see the Supporting Information). Unfortunately, the desired bicyclic intermediate **3d** could not be observed, even when using 1 equiv of isocyanide. More clear-cut evidence arises from the reaction of ^{t}BuNC with **1a**. At room temperature, addition of ^{t}BuNC to a solution of **1a** results *immediately* in a mixture of bicylobutane **3a** and cyclobutene **2a**. Upon standing at room temperature, the **3a** present in the mixture slowly (several days) converts to the thermodynamic product **2a**. When the reaction is performed at −94 °C, only the kinetic product **3a** (see the Supporting Information) is observed. Samples of isolated **3a** also rearrange to **2a** over several days at room temperature (see the Supporting Information). The concurrent formation of **3a** and **2a** followed by the slow rearrangement of **3a** to **2a** suggests that **3a** is unlikely to be an intermediate in the formation of **2a**. Instead, we propose that **3a** and **2a** are formed competitively from irreversible insertion into a Si−Si single bond (giving **2a**) and reversible cycloaddition to the Si=Si double bond of **1a** (giving **3a**) (Scheme 2). The principal possibility of a reversible reaction of isocyanides with Si=Si double bonds has recently been demonstrated.[14]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Text, figures, tables, and CIF files giving experimental procedures and spectral data for **2**−**4**, computational results for **I** and **II**, and crystallographic data including atomic positional and thermal parameters for **2a**,**d**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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